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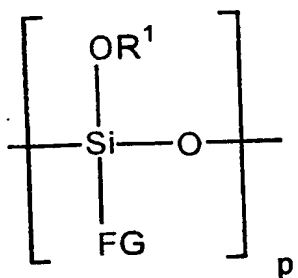
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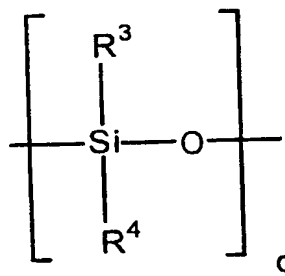
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(54) Title: EPOXY ALKOXY SILOXANE OLIGOMERS



(A)



(B)

(57) Abstract: Polymerizable siloxane oligomers comprising a plurality of repeating units of formula (A) and at least one unit of formula (B) and terminating in a residue R<sup>2</sup> or R<sup>8</sup> are disclosed. In these formulae FG is a functional group, such as 2-(3,4-epoxycyclohexylethyl), and the R groups are alkyl, aryl, haloalkyl, aralkyl, alkoxy or aryloxy of 1 to 10 carbons. Processes for preparing the oligomers by hydrolysis/condensation of monomers of formula (RO)<sub>3</sub>Si FG and one or more alkoxy silane monomers of formula R<sup>3</sup>R<sup>4</sup>R<sup>8</sup>SiOR<sup>2a</sup> are also disclosed, as are polymers resulting from the cationic polymerization of the oligomers.

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## EPOXY ALKOXY SILOXANE OLIGOMERS

### Field of the Invention

The invention relates to epoxy alkoxy siloxane oligomers.

### Background of the Invention

5        In recent years, there has been considerable interest in the photo, e-beam  
and thermally-induced cationic polymerization of siloxane-containing monomers and  
oligomers. Such monomers and oligomers have considerable potential in a wide  
diversity of applications including: non-stick release coatings, adhesives, abrasion  
resistant coatings for plastics, fiber optic coatings, reinforced composites and  
10    optical waveguides. The photopolymerizations of various multifunctional  
monomers characteristically proceeds only to low conversions due to trapping of  
residual reactive functional groups within the rigid, crosslinked network as it is  
formed. In this regard, siloxane containing monomers exhibit anomalous behavior  
that has been attributed to the conformational flexibility of the siloxane (Si-O-Si)  
15    bond and to free volume effects.

Preparation of multifunctional alkoxy siloxanes is difficult to accomplish by  
prior art methods. While epoxy-functional trialkoxy silanes are commercially  
available as starting materials, condensation polymerization of multifunctional  
alkoxy silanes generally results in crosslinked gels. Typically, alkoxy silanes such

as tetraethoxysilane (TEOS) are subjected to acid or base catalyzed hydrolysis-  
condensation in the presence of controlled amounts of water to yield a gel. In most  
acid catalyzed sol-gel processes, HCl is used, while NaOH and  $\text{NH}_4\text{OH}$  are often  
employed as base catalysts. However, it is difficult to reproducibly make  
5 intermediate, soluble, low viscosity, fluid oligomers. When such materials are  
obtained, they exhibit poor pot-lives and they gel on standing, due to further  
condensation.

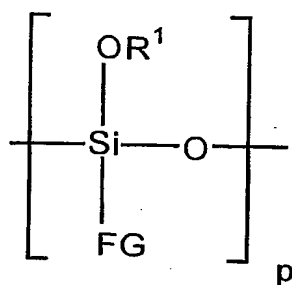
In addition, the basic hydrolysis catalysts used in the sol-gel reaction are  
strong inhibitors for cationic polymerizations, and the traces of basic catalysts that  
10 remain in the product inhibit subsequent cationic polymerizations. On the other  
hand, acid hydrolysis catalysts are not generally useful for the synthesis of epoxy-  
functional siloxanes, since epoxy groups undergo spontaneous ring-opening  
reactions with acids.

There is therefore a need for a process for making pure multifunctional  
15 alkoxy siloxane oligomers reproducibly and in good yield. There is also a need for  
alkoxy siloxane oligomers that have long pot-lives and low viscosity and that cure  
rapidly and completely. There is also a need for oligomers that can be polymerized  
to polymers having such desirable properties as: exhibiting no glass transition at  
temperatures below 300 °C; having a relatively low coefficient of thermal expansion  
20 (CTE) between 0-180°C; having a high storage modulus; and remaining stable at  
elevated temperatures.

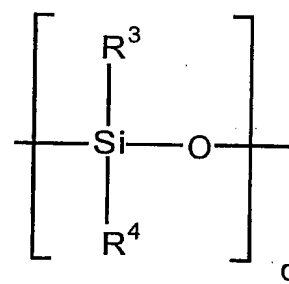
Summary of the Invention

In one aspect, the invention relates to a polymerizable siloxane oligomer comprising a plurality of repeating units of formula A and at least one unit of formula B:

5



A



B

and terminating in a residue  $\text{R}^2$  or  $\text{R}^8$ . In these formulae FG is a functional group. Each FG may be chosen from

linear, branched and cyclic alkyl residues of 1 to 20 carbons terminating in a 1-alkenyl ether;

10

linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens terminating in a 1-alkenyl ether;

linear, branched and cyclic alkyl residues of 1 to 20 carbons terminating in an acrylate, an alpha-chloroacrylate, an alpha-cyanoacrylate or a methacrylate;

15

linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens terminating in an acrylate, an alpha-chloroacrylate, an alpha-cyanoacrylate or a methacrylate;

linear, branched and cyclic alkyl residues of 1 to 20 carbons substituted with an epoxide;

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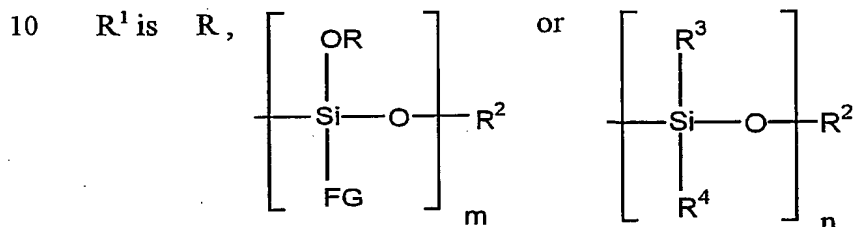
linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens substituted with an epoxide;

arylalkyl residues of 1 to 20 carbons substituted with an epoxide;

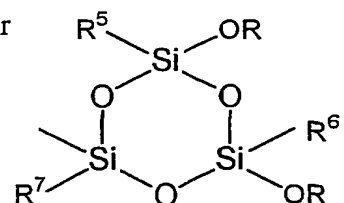
5 arylalkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens substituted with an epoxide; and

epoxy-functional organosiloxane residues of 1 to 20 silicons and 1 to 20 carbons.

R is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons;



$R^2$  is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons or



$R^3$  and  $R^4$  are independently alkyl, aryl, haloalkyl, aralkyl, alkoxy or aryloxy of 1 to 10 carbons;

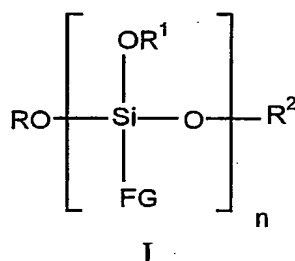
$R^5$ ,  $R^6$  and  $R^7$  are independently FG, alkyl, aryl, haloalkyl, aralkyl, alkoxy or aryloxy of 1 to 10 carbons;

15  $R^8$  is alkyl, aryl, haloalkyl, aralkyl, alkoxy or aryloxy of 1 to 10 carbons;

$m$  and  $n$  are independently 2 to 50;  $p$  is 2 to 50 and  $q$  is 1 to 50. Note that in this document, variables are defined when introduced and retain that definition throughout.

The foregoing oligomers may also be described in product-by-process terms as polymerizable siloxane oligomers produced by reacting one or more alkoxy silane monomers of formula  $(\text{RO})_3\text{Si FG}$  and one or more alkoxy silane monomers of formula  $\text{R}^3\text{R}^4\text{R}^8\text{SiOR}^{2a}$  with 0.5 to 2.5 equivalents of water, in the presence of an ion exchange resin, optionally in the presence of a solvent, and separating the resin from the siloxane oligomer. In these monomers,  $\text{R}^{2a}$  is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons.

In another aspect the invention relates to (1) polymers produced by cationically polymerizing one or more of the foregoing oligomers; and (2) polymers produced by cationically co-polymerizing one or more of the foregoing oligomers with an oligomer of formula:

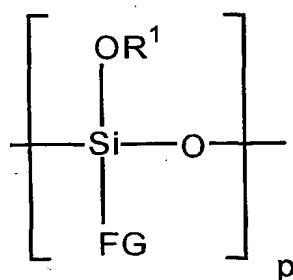


In another aspect the invention relates to a process for preparing a polymerizable siloxane oligomer comprising reacting one or more alkoxy silane monomers of formula  $(\text{RO})_3\text{Si FG}$  and one or more alkoxy silane monomers of formula  $\text{R}^3\text{R}^4\text{R}^8\text{SiOR}^{2a}$  with 0.5 to 2.5 equivalents of water, in the presence of an ion exchange resin, optionally in the presence of a solvent, and separating the resin from the siloxane oligomer. The ion exchange resin is preferably a quaternary ammonium resin.

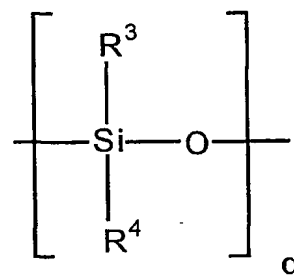


Detailed description of the Invention

The polymerizable siloxane oligomers of the invention are made up of a plurality of repeating units of formula A and at least one unit of formula B:

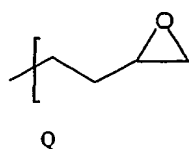
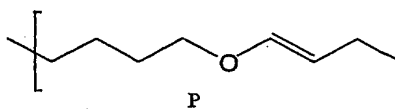
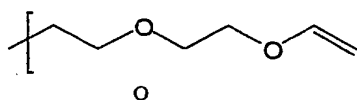
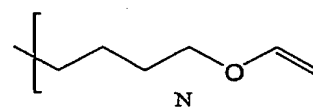
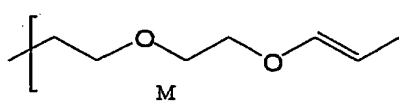
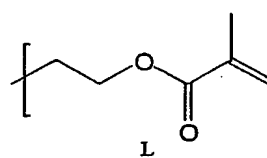
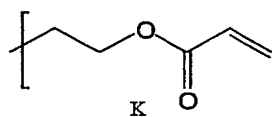
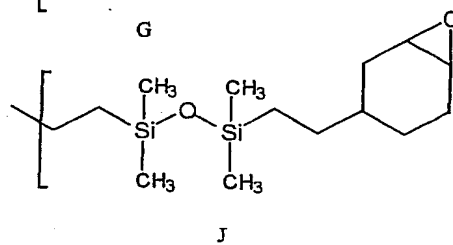
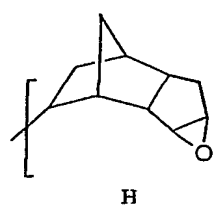
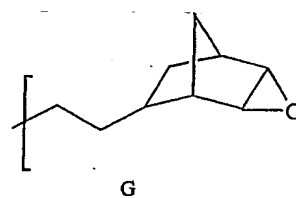
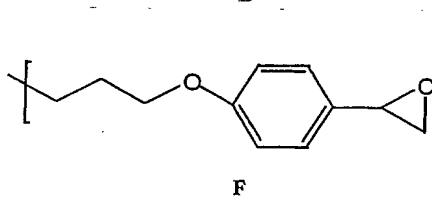
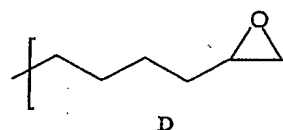
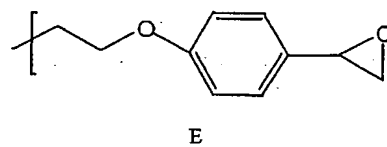
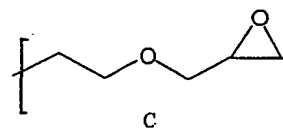
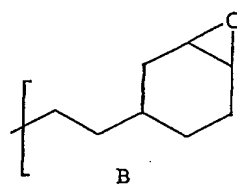
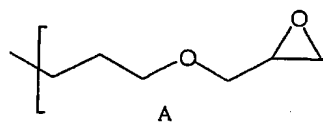


A



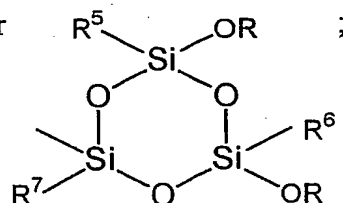
B

- 5 The oligomers of the invention may be block oligomers or random oligomers. Preferably the ratio of A to B (or p to q) is from 19:1 to 1:9, most preferably the ratio of A to B is from 1:1 to 3:1. In a preferred embodiment, FG is one or more residues chosen from formulae A-Q:



From among these residues, 2-(3,4-epoxycyclohexylethyl), 3-glycidoxypropyl and 1-propenoxy-2-ethoxyethyl are preferred. In another preferred embodiment, R<sup>1</sup> is methyl or ethyl; R<sup>2</sup> is

methyl, methoxy, ethyl, ethoxy, phenyl or

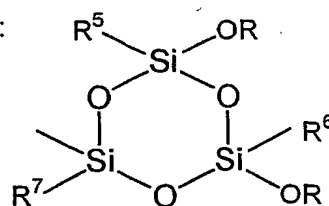


- 5 R<sup>3</sup>, R<sup>4</sup> and R<sup>8</sup> are chosen independently from methyl, methoxy, ethyl, ethoxy, and phenyl; and

R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are chosen independently from methyl, methoxy, ethyl, ethoxy, phenyl and FG.

- As will be apparent to the artisan, the ratios of residues represented by R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> in a random oligomer will reflect the ratio and relative reactivities of A to B in the monomer mix from which the oligomer was prepared.
- 10

The siloxanes of the invention are straight- or branched-chain oligomers and may additionally contain one or more cyclic structures composed of three monomer units as end groups, as depicted in the formula:



- 15 The presence of the ring structure is dependent on the number of equivalents of water employed in the reaction and on reaction conditions, including temperature and time. The oligomer chains are composed of from two to fifty siloxane monomer units, preferably of from two to twenty monomer units.

The effective molecular weight and viscosities of the oligomers of the invention may be varied according to the desired use, both of the oligomer and of the product polymer. For many purposes oligomers in which the sum of p and q is from 4 to 20 are preferred. The rate and extent of the hydrolysis-condensation reaction are dependent on the strength of the catalyst used. Strong acids or bases cause fast hydrolysis and condensation of alkoxysilanes and high conversions to oligomers. The reaction is well controlled with ion exchange resins as catalysts. Condensation in the presence of these catalysts proceeds at a convenient rate so that the reaction times are not inordinately long and at the same time slow enough that adequate control can be maintained over the reaction to provide reproducible molecular weight control and to avoid gelation.

The polymerizable siloxanes of the invention are synthesized by base-catalyzed hydrolysis and subsequent condensation of an alkoxy silane monomer of Formula  $(RO)_3SiFG$  and one or more alkoxy silane monomers of formula  $R^3R^4R^8SiOR^{2a}$ . In the above formula, it is preferred that the alkoxy group (RO) is methoxy or ethoxy and that the functional group FG not be polymerizable at a rate comparable to that of the alkoxy siloxane. As defined above,  $R^{2a}$  is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons and  $R^3$ ,  $R^4$  and  $R^8$  are independently alkyl, aryl, haloalkyl, aralkyl, alkoxy or aryloxy of 1 to 10 carbons. Preferably,  $R^{2a}$  is methyl or ethyl and  $R^3$ ,  $R^4$  and  $R^8$  are chosen independently from methyl, methoxy, ethyl, ethoxy, and phenyl. Monomers that provide the "B" units include: tetraethoxysilane (ethylorthosilicate), tetramethoxysilane (methylorthosilicate), tetraisopropoxysilane, methyltrimethoxysilane, ethyltriethoxysilane, hexyltriethoxysilane, cyclohexyltrimethoxysilane, 1,1,1-trifluoroethyltriethoxysilane, phenyltriethoxysilane, phenylmethyldiethoxysilane, phenylmethyldimethoxysilane, diphenyldimethoxysilane, 2-phenylethyltrimethoxysilane, benzyltriethoxysilane, vinyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane,

diethyldimethoxysilane, allyltrimethoxysilane, divinyltrimethoxysilane, methyvinyltrimethoxysilane, bis(triethoxysilyl)methane, bis(triethoxysilyl)ethane, butenyltrimethoxysilane, 3-bromopropyltrimethoxysilane, 2-chloroethylmethyldimethoxysilane, 1,1,2,2-tetramethoxy-1,3-dimethyldisiloxane, 5 phenyltrimethoxysilane. Also, useful in these mixtures are trimethoxysilyl-terminated polydimethylsiloxanes as well as the corresponding hydroxyl-terminated polydimethylsiloxanes. The foregoing monomers are either commercially available or readily synthesized by reactions well known in the art.

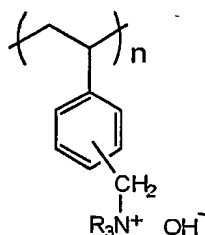
The ion exchange resin catalyzed sol-gel copolycondensation can be 10 conducted simultaneously with all the components to provide a random distribution of the resulting repeating units derived from **A** and **B** in the oligomer. Alternatively, the reaction can be conducted in a sequential fashion. In this latter case, a second alkoxy silane of either structure **A** or **B** is added after the first substrate has been consumed by reaction. This results in an oligomer in which like repeating units 15 occur together in a block structure.

The reaction is typically carried out in a solvent in which both the starting silane monomer and the siloxane product are soluble. Alcohols such as ethanol, t-butanol, n-propanol and isopropanol are preferred.

The reaction may be conducted at temperatures sufficient to maximize the 20 rate of reaction while minimizing undesirable side reactions, generally from 0-100°C and preferably from 35-70°C. At higher temperatures, the reaction is completed in a shorter time. For example, a reaction conducted at 45°C may be complete at 24 hours, while a similar reaction carried out at 60°C is complete in 12 hours. The extent of reaction may be determined by <sup>1</sup>H NMR spectroscopy, by 25 monitoring the consumption of alkoxy groups

The degree of condensation may be controlled by varying the ratio of water to silane in the reaction mixture. Higher ratios of water result in an increase in the rate of the hydrolysis-condensation reaction and also in a greater proportion of oligomers with higher molecular weights. For example, reactions at 60°C with 1.0 and 1.5 equivalents of water will result in a broad distribution of oligomeric products in both cases, with a greater proportion of higher molecular weight material in reactions with 1.5 equivalents than in reactions with 1.0 equivalents of water. For some uses, the viscosity of the oligomer may be from 100 to 1,000,000 cps; for other uses, oligomers having a viscosity of 500 cps to 5000 cps are preferred; for yet other uses, the reaction is carried to high molecular weight, and the oligomer which is isolated is a very high viscosity liquid or a glassy solid. One set of preferred oligomers according to the process has an apparent molecular weight of 3000 to 10,000.

Various basic ion exchange resins may be employed as catalysts in the processes of this invention. For example, strongly basic ion exchange resins such as Amberlite A-27, Amberlite IRA-400 and Amberlite IRA-904 from Rohm and Haas Corp. having the structure depicted below have been employed.



Most advantageously, the ion exchange resin is in a crosslinked bead form that permits recovery from the reaction mixture by simple filtration. The ion-exchange resin catalyst may be reused in subsequent sol-gel reactions. Alternatively, the condensations may be carried out in a continuous fashion on a fixed bed of the resin. The hydrolysis/condensation reaction does not appear limited by porosity or ion-exchange capacity of the resin. Exemplary styrene-divinyl benzene resins useful

in the practice of the invention are Amberlyst® and Amberlite®, Rohm & Haas Company; Ionac®, Sybron Chemicals; Dowex®, Dow Chemical; NRW®, Purolite; Tulsion®, Thermax, Ltd; and the CG and SBG lines of resins from Resintech, Inc. Removal of the catalyst prevents further reaction of the oligomer leading to

5 crosslinking, and results in a product which retains its initial viscosity during storage. The oligomers of the invention possess good shelf stability, showing no increase in viscosity on standing for more than two months.

After removal of the solvent, the resulting multifunctional siloxane oligomers may be further polymerized via the functional groups FG by various

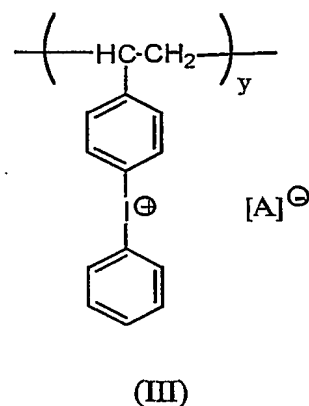
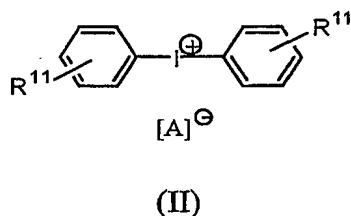
10 means. For example, the epoxy functional oligomers may be combined with amine or anhydride curing agents and polymerized by traditional thermal methods. Acrylate and methacrylate functional oligomers may be similarly thermally cured through the use of peroxide and azo free radical initiators. Alternatively, these oligomers may be also photopolymerized. Epoxy, 1-propenyl ether, 1-butenyl ether

15 and vinyl ether functional oligomers can be photopolymerized using UV or visible irradiation in the presence of diaryliodonium, dialkylphenacylsulfonium, triarylsulfonium salt, and ferrocenium salt photoinitiators. The aforementioned oligomer-photoinitiator mixtures may be also effectively cured in the presence of the above onium salts using e-beam irradiation. By the use of the proper onium catalyst

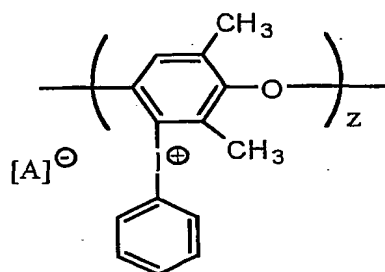
20 and/or the addition of copper compounds as co-catalysts, the oligomers may be thermally cured. Acrylate and methacrylate oligomers may be photopolymerized using a plethora of free radical photoinitiators including for example, benzoin, benzoin alkyl ethers, 1,1-diethoxyacetophenone, 1-benzoylcyclohexanol and many others.

The oligomers and the polymers resulting from the polymerization of the oligomers of the invention have many applications. For example, the polymers may be employed as protective and abrasion resistant coatings for wood, metals, plastics and glass. They may be employed as adhesive or bonding agents.

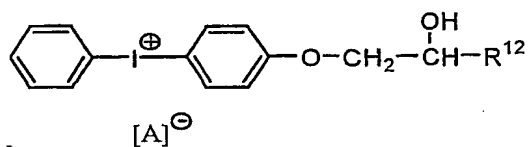
- 5 Combined with fibrous reinforcing agents the oligomers may be cured by UV and e-beam radiation and/or heat to give high performance composites. They may be further used as curable encapsulating and potting agents for electronic and microelectronic applications. Further uses lie in resins for stereolithography, holographic recording media and as optical adhesives, fiber optic coatings, waveguides in photonic applications and for other applications requiring high mechanical strength, stability at high temperatures, and high rate of cure. In the course of their use in various applications, the oligomers may be combined with various fibrous or particulate reinforcing agents, flow control and flatting agents, photosensitizers, pigments and dyes and mold releases.
- 10
- 15 The cationic polymerization initiator is preferably a diazonium, sulfonium, phosphonium, or iodonium salt. A preferred initiator is a diaryliodonium salt selected from the group having formulae (II), (III), (IV), and (V)







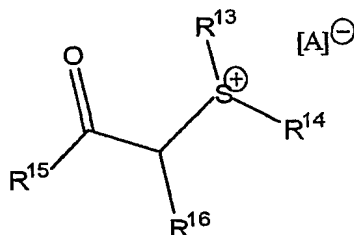
(IV)



(V)

wherein each  $R^{11}$  is independently hydrogen,  $C_1$  to  $C_{20}$  alkyl,  $C_1$  to  $C_{20}$  alkoxy,  $C_1$  to  $C_{20}$  hydroxyalkoxy, halogen, and nitro;  $R^{12}$  is  $C_1$  to  $C_{30}$  alkyl or  $C_1$  to  $C_{30}$  cycloalkyl; y and z are each independently integers having a value of at least 5;  $[A]^\ominus$  is a non-nucleophilic anion, commonly  $SbF_6^\ominus$ ,  $BF_4^\ominus$ ,  $PF_6^\ominus$ ,  $AsF_6^\ominus$ , or  $(C_6F_5)_4B^\ominus$ .

Another preferred cationic polymerization initiator is a phenylacetylsulfonium salt having formula (VI)



(VI)

wherein  $R^{13}$  is a  $C_1$  to  $C_{30}$  monovalent organic radical;  $R^{14}$  is a  $C_1$  to  $C_{30}$  monovalent organic radical, or  $R^{13}$  and  $R^{14}$  taken together may form a 5 or 6-membered ring;  $R^{15}$  is  $C_6$  to  $C_{20}$  alkyl, aryl,  $C_6$  to  $C_{20}$  substituted alkyl or substituted aryl;  $R^{16}$  is hydrogen or  $C_1$  to  $C_8$  alkyl; and  $[A]^\ominus$  is a non-nucleophilic anion, such as previously listed.  $R^{14}$  may also be a photosensitizing residue.

Thermal cure of the epoxy resin can be effected through the use of the cationic polymerization initiator with or without the addition of a copper co-catalyst (accelerator). Furthermore, by changing the structures of the materials included with the oligomer and by varying their concentrations, the onset curing temperature and the speed of cure can be adjusted within a wide latitude. Curing can alternatively be induced by irradiation of the cationic polymerization initiator/epoxy resin by UV light (or at longer wavelengths as discussed below) or by e-beam. E-beam curing is described in U.S. patents 5,260,349 and 4,654,379. Curing agents are described in U.S. Patents 4,842,800, 5,015,675, 5,095,053, and 5,073,643.

Preferred diaryliodonium salts are [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate, wherein in structure (V),  $[A]^{\ominus}$  is  $SbF_6^{\ominus}$ , and  $R^{12}$  is  $C_{12}H_{25}$  (available from Polyset Company, Mechanicville, New York, as PC-2506); and wherein in structure (V),  $[A]^{\ominus}$  is  $PF_6^{\ominus}$ , and  $R^1$  is  $C_{12}H_{25}$  (available from Polyset Company as PC2508). Triarylsulfonium salts, such as the mixture of S,S-diphenyl-4-thiophenoxyphenylsulfonium hexafluoroantimonate and bis(diphenylsulfonio)4,4'-diphenylsulfide bishexafluoroantimonate are commercially available from Polyset Company as PC2505. Dialkylphenacylsulfonium salts having the general formula (VI) are disclosed in pending U.S. Patent Application Serial No. 09/208,265 filed December 8, 1998. The disclosures of the foregoing patents and application are incorporated herein by reference.

#### Definitions:

"Alkyl" is intended to include linear, branched, or cyclic hydrocarbon structures and combinations thereof. "Lower alkyl" refers to alkyl groups having from 1 to 4 carbon atoms. Examples of lower alkyl groups include methyl, ethyl, propyl, isopropyl, butyl, s-and t-butyl and the like. Preferred alkyl groups are those of  $C_{20}$  or below. "Cycloalkyl" is a subset of alkyl and includes cyclic hydrocarbon groups of from 3 to 8 carbon atoms. Examples of cycloalkyl groups include c-propyl, c-butyl, c-pentyl, c-hexyl, norbornyl and the like.

"Alkoxy" or "alkoxyl" refers to groups of from 1 to 20 carbon atoms of a straight, branched, cyclic configuration and combinations thereof attached to the parent structure through an oxygen. Examples include methoxy, ethoxy, propoxy, isopropoxy, cyclopropyloxy, cyclohexyloxy and the like. "Lower-alkoxy" refers to groups containing one to four carbons.

"Acyl" refers to groups of from 1 to 20 carbon atoms of a straight, branched, cyclic configuration, saturated, unsaturated and aromatic and combinations thereof, attached to the parent structure through a carbonyl functionality. Examples include acetyl, benzoyl, propionyl, isobutyryl, *t*-butoxycarbonyl, benzyloxycarbonyl and the like. "Lower-acyl" refers to groups containing one to four carbons.

"Aryl" refers to a 5- or 6-membered aromatic ring; a bicyclic 9- or 10-membered, partially or fully aromatic ring system; or a tricyclic 13- or 14-membered partially or fully aromatic ring system optionally substituted with 1-3 lower alkyl, halo lower alkyl, = O, -NO<sub>2</sub>, halogen, hydroxy, alkoxy, cyano, phenyl, benzyl, phenoxy or benzyloxy. The aromatic 6- to 14-membered carbocyclic rings include, *e.g.*, benzene, naphthalene, indane, tetralin, and fluorene.

"Arylalkyl" means an alkyl residue attached to an aryl ring. Examples are benzyl, phenethyl and the like.

The following examples are included by way of exemplification and are not intended to imply any limitation.

Examples 1 and 2: Sol-gel condensations of 2-(3,4-epoxycyclohexylethyl)-trimethoxysilane

Preparations of O1 and O2

A 50 mL round bottom flask fitted with a magnetic stirrer, reflux condenser and a thermometer was charged with 246.4 g (1 mol) of 2-(3,4-epoxycyclohexylethyl)-trimethoxysilane, 1.5 equivalents (27 g) of deionized water, 8 g of Amberlite IRA-400 ion exchange resin, and 50 mL of isopropanol. The

colorless solution was stirred and heated at reflux ( $\sim 80^{\circ}\text{C}$ ) for 4 hours (**O2**) and 6 hours (**O1**). After the designated reaction time, the solvent was removed under reduced pressure and the resulting in a colorless, viscous liquid. Oligomers were further characterized by  $^1\text{H}$  NMR spectroscopy and by RTIR analysis.

5    Examples 3-6 : Sol-gel condensations of 2-(3,4-epoxycyclohexylethyl)trimethoxysilane with methyltrimethoxysilane, phenyltrimethoxysilane, methyl phenyldimethoxysilane and diphenyldimethoxysilane.

In a manner similar to examples 1 and 2, there were combined in a 500 mL round bottom flask fitted with a magnetic stirrer, reflux condenser and a  
10    thermometer, 0.7 equivalents (172.5 g) of 2-(3,4-epoxycyclohexylethyl)trimethoxy silane and 0.3 equivalents of methyltrimethoxysilane (to produce oligomer **O3**), phenyltrimethoxysilane (to produce oligomer **O4**), 0.3 equivalents of methyl phenyldimethoxysilane (to produce oligomer **O5**) or 0.3 equivalents of diphenyldimethoxysilane (to produce oligomer **O6**). To this mixture was added 1.5  
15    equivalents (27g) of deionized water, 8 g of Amberlite IRA-400 ion exchange resin, and 50 mL of iso propanol. The colorless solution was stirred and heated at reflux ( $\sim 80^{\circ}\text{C}$ ) for 22 hours for **O3** and 12 hours for **O4**, **O5** and **O6**. After the designated reaction time, the solvent was removed under reduced pressure and the resulting colorless, viscous liquid oligomers were obtained.

20    Examples 7-10: Thermal polymerization of oligomers **O3-O6**.

To each of the above resins was added 2% by weight of a 50% solution of 4(2-hydroxy-1-tetradecyloxyphenyl)phenyliodonium hexafluoroantimonate dissolved in 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate (Union Carbide ERL-4221E). Four grams of the mixture was placed into a shallow  
25    aluminum pan and the pan placed in a forced air oven at  $165^{\circ}\text{C}$  for 1.5 hours. Transparent, colorless cured resin castings were obtained. The cured samples were

removed from the pan and then cut into bar specimens for mechanical and thermal testing. The results of those tests are given in Table 1.

In general, the modified resins (O3-O6) display comparable mechanical and thermal characteristics to the unmodified resins (O1 and O2) and, in addition,  
 5 display better resistance to cracking and crazing. The very small changes of the CTE values throughout the temperature range from 0-200°C are indicative of a very highly crosslinked system.

Table 1

## Results of Mechanical and Thermal Testing of Resins

Property	O3	O2	O4	O5	O6	O1
<u>Curing Characteristics</u>						
cracking	-	minor	no	no	no	minor
crazing	-	minor	minor	no	no	yes
separation	-	yes	yes	yes	yes	yes
<u>DSC Cure*</u>						
$\Delta H$ (J/g)	171	312	300	322	280	283
onset (°C)	182	160	140	140	140	170
Peak (°C)	191	168	160	163	167	182
peak height (MW)	38	34	24	18	15	49
<u>CTE<sup>#</sup></u>						
0-100 (°C)	95	80	107	105	95	65
0-200 (°C)	105	92	128	120	110	73
100-200 (°C)	115	104	150	139	125	83
<u>Storage Modulus</u>						
25°C (GPa)	0.850	.850	1.16	0.925	0.820	1.6
150°C (GPa)	0.650	0.720	0.53	0.520	0.480	1.3
$\Delta$ (MPa) <sup>†</sup>	200	130	630	405	340	300
<u>Viscosity</u>						
@ 25°C (cps)	78000	23000	11500	30200	semisolid	semisolid
@ 65°C (cps)	3617	1320	-	-	15500	14000

\*Heating rate 10°C/min in air. <sup>#</sup>Coefficient of thermal expansion. <sup>†</sup>Change in modulus from 25-150 °C.

Examples 11-16 Mixtures of Modified and Unmodified Resins

Combined and thermally cured were 50/50 wt% mixtures of **O1** or **O2** with modified resins **O4-O6**. The compositions are given in Table 2. The mechanical and thermal properties are depicted in Table 3.

5

**Table 2****Compositions of Mixed Oligomers**

<b>Example</b>	<b>11</b>	<b>12</b>	<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>
<b>O1</b>	50	50	50	-	-	-
<b>O2</b>	-	-	-	50	50	50
<b>O4</b>	50	-	-	50	-	-
<b>O5</b>	-	50	-	-	50	-
<b>O6</b>	-	-	50	-	-	50

10

The thermal and mechanical properties of the thermally cured mixtures of **O1** or **O2** with the modified resins **O4-O6** are excellent.

**Table 3**  
**Results of Mechanical and Thermal Testing of Resins Mixtures**

Property	11	12	13	14	15	16
<u>Curing Characteristics</u>						
Cracking	no	no	no	no	no	no
Separation	yes	yes	yes	yes	yes	yes
Crazing	minor	no	no	yes	no	no
	-					
<u>DSC Cure*</u>						
$\Delta H$ (J/g)	254	241	244	245	244	243
onset ( $^{\circ}\text{C}$ )	140	160	160	160	160	160
Peak ( $^{\circ}\text{C}$ )	173	179	180	174	177	177
Peak height	39	41	39	56	37	39
<u>CTE<sup>#</sup></u>						
0-100 ( $^{\circ}\text{C}$ )	104	98	80	112	105	100
0-200 ( $^{\circ}\text{C}$ )	116	108	90	122	115	110
100-200 ( $^{\circ}\text{C}$ )	127	118	100	132	125	120
<u>Storage Modulus</u>						
25 $^{\circ}\text{C}$ (GPa)	1.2	1.3	1.4	1.2	1.25	1.2
150 $^{\circ}\text{C}$ (GPa)	0.746	0.889	1.01	0.765	0.849	0.849
$\Delta$ (MPa) <sup>†</sup>	451	422	390	440	397	357

\*Heating rate 10 $^{\circ}\text{C}/\text{min}$  in air. <sup>#</sup>Coefficient of thermal expansion. <sup>†</sup>Change in modulus from 25-150  $^{\circ}\text{C}$ .

#### Example 17 - amine cure

To 10 g of a resin (04) prepared by the condensation of 3 parts of phenyltrimethoxysilane and 7 parts of 4(2-trimethoxysilylethyl)epoxycyclohexane there were added 3.5 g Epi-cure 826 amine hardener from the Shell Company. The

blend was thoroughly mixed, poured into a shallow pan and then allowed to stand at 50° for 1 hour in a forced air oven. At the end of this time, the reaction mixture was found to consist of a hard, insoluble, crosslinked resin.

Example 18 - anhydride cure

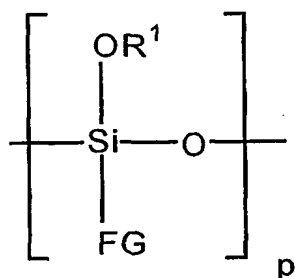
To 10 g of a resin (05) prepared by the condensation of 3 parts of diphenyldimethoxysilane and 7 parts of 4(2-trimethoxysilylethyl)epoxycyclohexane there were added 3.5 g hexahydrophthalic anhydride. The blend was thoroughly mixed, poured into a shallow pan and then allowed to stand at 165° for 1 hour in a forced air oven. At the end of this time, the reaction mixture was found to consist of a hard, insoluble, crosslinked resin.



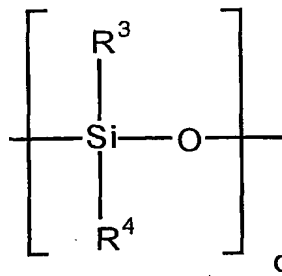
## CLAIMS

I claim:

1. A polymerizable siloxane oligomer comprising a plurality of repeating units of formula A and at least one unit of formula B:



A



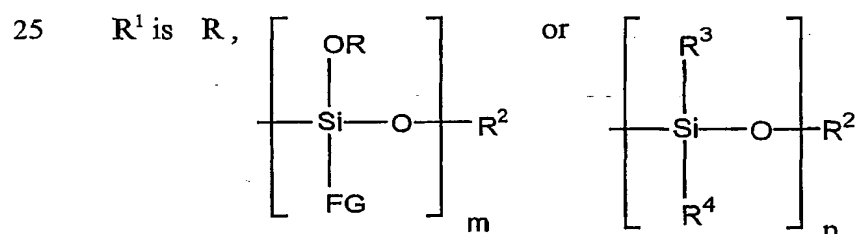
B

and terminating in a residue  $\text{R}^2$  or  $\text{R}^8$ , wherein

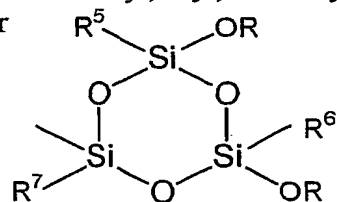
- 5 FG is a functional group and each FG in said oligomer is independently chosen from linear, branched and cyclic alkyl residues of 1 to 20 carbons terminating in a 1-alkenyl ether;  
 linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens terminating in a 1-alkenyl ether;  
 10 linear, branched and cyclic alkyl residues of 1 to 20 carbons terminating in an acrylate, an alpha-chloroacrylate, an alpha-cyanoacrylate or a methacrylate;  
 linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens terminating in an acrylate, an alpha-chloroacrylate, an alpha-cyanoacrylate or a methacrylate;  
 15 linear, branched and cyclic alkyl residues of 1 to 20 carbons substituted with an epoxide;  
 linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens substituted with an epoxide;  
 arylalkyl residues of 1 to 20 carbons substituted with an epoxide;

- 20 arylalkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens substituted with an epoxide; and  
epoxy-functional organosiloxane residues of 1 to 20 silicons and 1 to 20 carbons;

R is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons;



$R^2$  is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons  
or



$R^3$  and  $R^4$  are independently alkyl, aryl, haloalkyl, aralkyl, alkoxy or aryloxy of 1 to 10 carbons;

- 30  $R^5$ ,  $R^6$  and  $R^7$  are independently FG, alkyl, aryl, haloalkyl, aralkyl, alkoxy or aryloxy of 1 to 10 carbons;

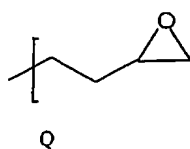
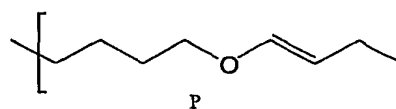
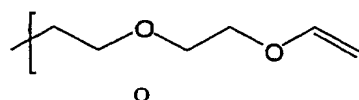
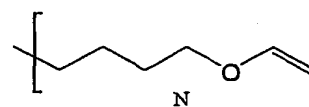
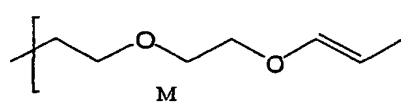
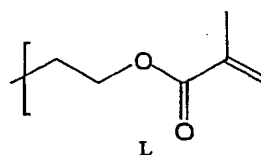
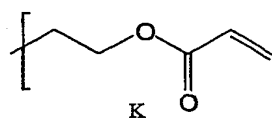
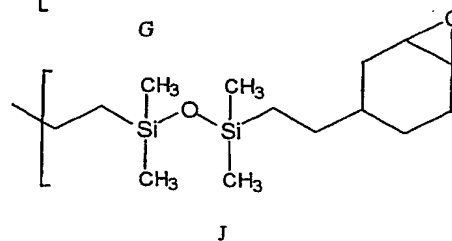
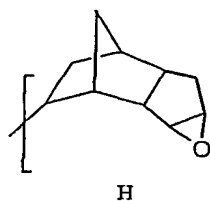
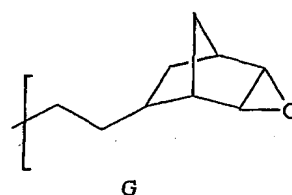
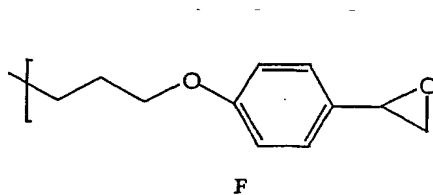
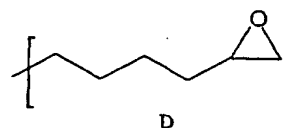
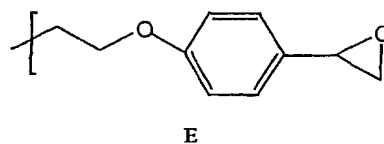
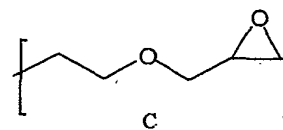
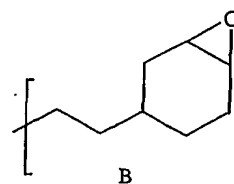
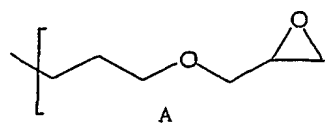
$R^8$  is alkyl, aryl, haloalkyl, aralkyl, alkoxy or aryloxy of 1 to 10 carbons;

m and n are independently 2 to 50; and

p is 2 to 50.

- 35 q is 1 to 50.

2. A block oligomer according to claim 1.
3. A random oligomer according to claim 1.
4. An oligomer according to claim 1 wherein the ratio of A to B is from 19:1 to 1:9.
5. An oligomer according to claim 1 wherein the ratio of A to B is from 1:1 to 3:1.
6. An oligomer according to claim 1 wherein each FG has a structure independently chosen from the group consisting of residues of formulae A-Q:

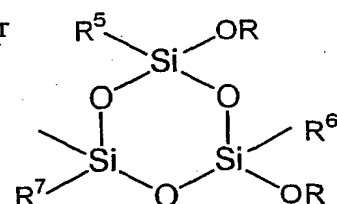


7. An oligomer according to claim 1, wherein each FG is independently 2-(3,4-epoxycyclohexylethyl), 3-glycidoxypropyl, or 1-propenoxy-2-ethoxy ethyl.

8. An oligomer according to claim 1, wherein:

R<sup>1</sup> is methyl or ethyl;

R<sup>2</sup> is methyl, methoxy, ethyl, ethoxy, phenyl or



R<sup>3</sup>, R<sup>4</sup> and R<sup>8</sup> are chosen independently from methyl, methoxy, ethyl, ethoxy, and phenyl; and

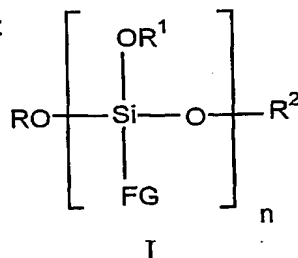
R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are chosen independently from methyl, methoxy, ethyl, ethoxy, phenyl and FG.

9. An oligomer according to claim 1, wherein the sum of p and q is from 4 to 20.

10. A polymer produced by cationically polymerizing an oligomer according to claim 1.

11. A polymer produced by cationically co-polymerizing an oligomer according to claim 1

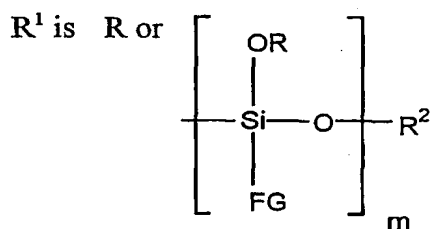
and an oligomer of formula:



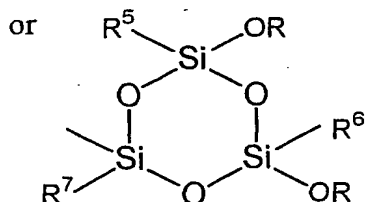
wherein

- FG is a functional group and each FG in said oligomer is independently chosen from
- 5 linear, branched and cyclic alkyl residues of 1 to 20 carbons terminating in a 1-alkenyl ether;
- linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens terminating in a 1-alkenyl ether;
- linear, branched and cyclic alkyl residues of 1 to 20 carbons terminating in
- 10 an acrylate, an alpha-chloroacrylate, an alpha-cyanoacrylate or a methacrylate;
- linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens terminating in an acrylate, an alpha-chloroacrylate, an alpha-cyanoacrylate or a methacrylate;
- linear, branched and cyclic alkyl residues of 1 to 20 carbons substituted with
- 15 an epoxide;
- linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens substituted with an epoxide;
- arylalkyl residues of 1 to 20 carbons substituted with an epoxide;
- arylalkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens substituted
- 20 with an epoxide; and
- epoxy-functional organosiloxane residues of 1 to 20 silicons and 1 to 20 carbons;

R is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons;



25  $R^2$  is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons



and m and n are independently 2 to 50.

12. A polymer produced by e-beam polymerization of an oligomer according to claim 1.

13. A polymer produced by polymerizing an oligomer according to claim 1 with an amine or anhydride.

14. A polymerizable siloxane oligomer produced by reacting one or more alkoxy silane monomers of formula  $(RO)_3Si$  FG and one or more alkoxy silane monomers of formula  $R^3R^4R^8SiOR^{2a}$  wherein:

FG has a structure independently chosen for each monomer from the group

5 consisting of:

linear, branched and cyclic alkyl residues of 1 to 20 carbons terminating in a 1-alkenyl ether;

linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens terminating in a 1-alkenyl ether;

10 linear, branched and cyclic alkyl residues of 1 to 20 carbons terminating in an acrylate, an alpha-chloroacrylate, an alpha-cyanoacrylate or a methacrylate;

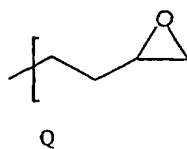
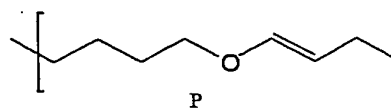
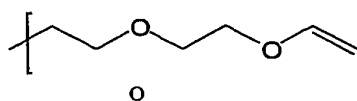
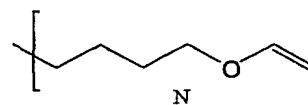
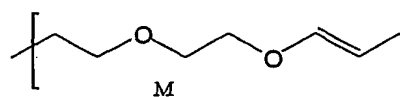
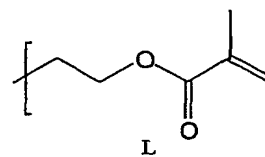
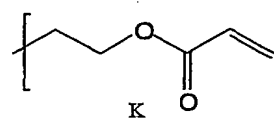
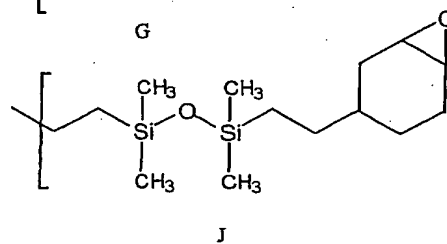
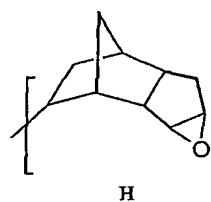
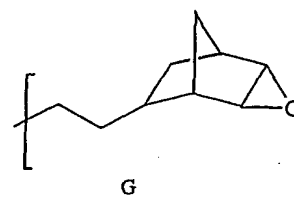
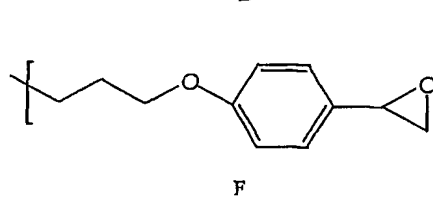
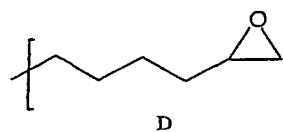
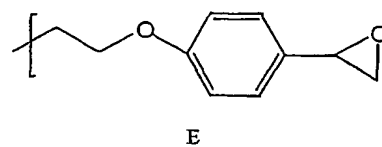
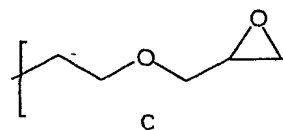
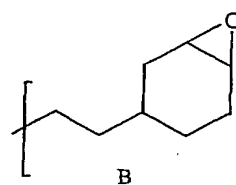
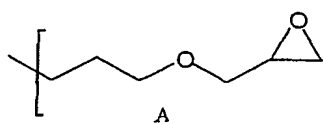
linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens terminating in an acrylate, an alpha-chloroacrylate, an alpha-cyanoacrylate or a methacrylate;

- 15 linear, branched and cyclic alkyl residues of 1 to 20 carbons substituted with an epoxide;  
linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens substituted with an epoxide;  
arylalkyl residues of 1 to 20 carbons substituted with an epoxide;  
20 arylalkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens substituted with an epoxide; and  
epoxy-functional organosiloxane residues of 1 to 20 silicons and 1 to 20 carbons;  
R is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons;  
25 R<sup>2a</sup> is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons;  
R<sup>3</sup>, R<sup>4</sup> and R<sup>8</sup> are independently alkyl, aryl, haloalkyl, aralkyl, alkoxy or aryloxy of 1 to 10 carbons;  
with 0.5 to 2.5 equivalents of water, in the presence of an ion exchange resin, optionally in the presence of a solvent, and separating the resin from said siloxane  
30 oligomer.

15. A polymerizable oligomer according to claim 14 having a molecular weight between 3000 and 10,000.

16. A polymerizable siloxane oligomer according to claim 14, wherein FG has a structure independently chosen for each monomer from the group consisting of the structures of Formulae A-Q:





17. A polymerizable siloxane oligomer according to claim 14, wherein FG for each monomer is independently 2-(3,4-epoxycyclohexylethyl) or 3-glycidoxypropyl.

18. A polymerizable siloxane oligomer according to claim 14, wherein R is methyl or ethyl and  $R^3$ ,  $R^4$  and  $R^8$  are chosen independently from methyl, methoxy, ethyl, ethoxy, and phenyl.

19. A process for preparing a polymerizable siloxane oligomer comprising: reacting one or more alkoxy silane monomers of formula  $(RO)_3Si$  FG and one or more alkoxy silane monomers of formula  $R^3R^4R^8SiOR^{2a}$  wherein FG has a structure independently chosen for each monomer from the group consisting of:

5 linear, branched and cyclic alkyl residues of 1 to 20 carbons terminating in a 1-alkenyl ether;

linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens terminating in a 1-alkenyl ether;

10 linear, branched and cyclic alkyl residues of 1 to 20 carbons terminating in an acrylate, an alpha-chloroacrylate, an alpha-cyanoacrylate or a methacrylate;

linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens terminating in an acrylate, an alpha-chloroacrylate, an alpha-cyanoacrylate or a methacrylate;

15 linear, branched and cyclic alkyl residues of 1 to 20 carbons substituted with an epoxide;

linear, branched and cyclic alkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens substituted with an epoxide;

arylalkyl residues of 1 to 20 carbons substituted with an epoxide;

20 arylalkyl ether residues of 1 to 20 carbons and 1 to 9 oxygens substituted with an epoxide; and

epoxy-functional organosiloxane residues of 1 to 20 silicons and 1 to 20 carbons;

R is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons;

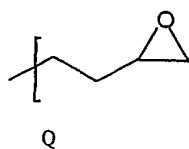
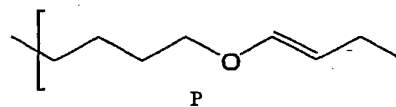
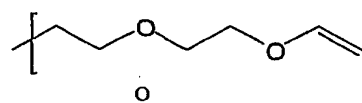
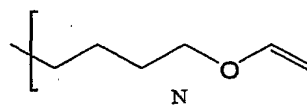
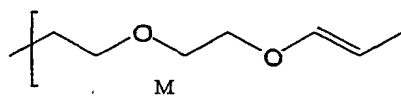
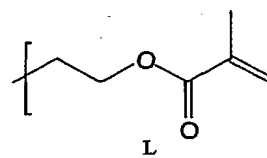
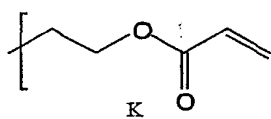
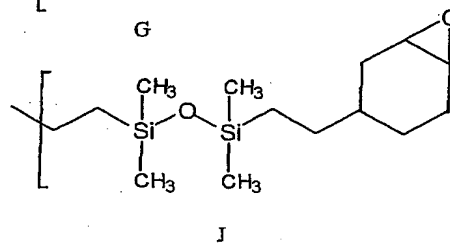
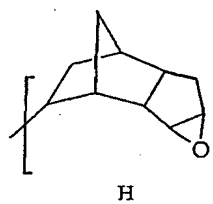
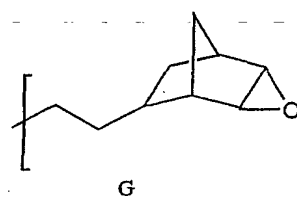
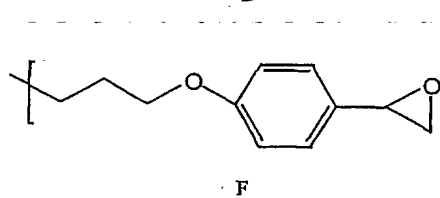
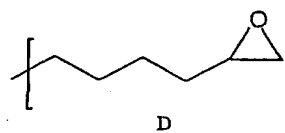
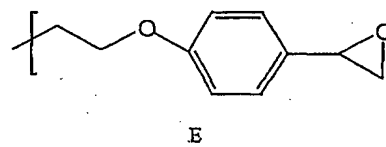
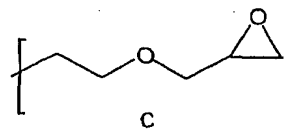
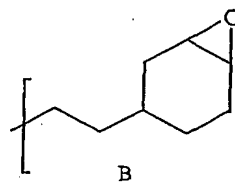
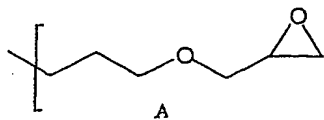
R<sup>2a</sup> is alkyl, aryl, haloalkyl or aralkyl of 1 to 10 carbons;

25 R<sup>3</sup>, R<sup>4</sup> and R<sup>8</sup> are independently alkyl, aryl, haloalkyl, aralkyl, alkoxy or aryloxy of 1 to 10 carbons;

with 0.5 to 2.5 equivalents of water, in the presence of an ion exchange resin, optionally in the presence of a solvent, and separating the resin from said siloxane oligomer.

20. A process according to claim 19 wherein said ion exchange resin is a quaternary ammonium resin.

21. A process according to claim 19, wherein FG has a structure independently chosen for each monomer from the group consisting of the structures of Formulae A-Q:



22. A process according to claim 19, wherein R is methyl or ethyl and R<sup>3</sup>, R<sup>4</sup> and R<sup>8</sup> are chosen independently from methyl, methoxy, ethyl, ethoxy, and phenyl.

## INTERNATIONAL SEARCH REPORT

Intern al application No.

PCT/US00/08666

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : C08G 77/08, 77/18, 77/20

US CL : 528/418, 421, 32, 33, 41; 556/458; 549/215; 526/279

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/418, 421, 32, 33, 41; 556/458; 549/215; 526/279

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,650,474 A (YAMAYA et al.) 22 July 1997 (22/07/97) col. 3, lines 35-50, col. 4, lines 8-11	1, 3-9, 14-18
Y	US 6,011,079 A (DOUGHERTY et al.) 04 January 2000 (04/01/00) col. 1, lines 32-33	10
Y	US 5,035,894 A (LEE et al.) 30 July 1991 (30/07/91) col. 4, lines 52-57, col. 8, lines 18-20	12
A,E	US 6,046,276 A (AMBROSE et al.) 04 April 2000 (04/04/00) col. 7, lines 55-56, col. 8, lines 1-2	13
A,E	US 6,069,259 A (CRIVELLO) 30 May 2000 (30/05/00)	1-22

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

15 JUNE 2000

Date of mailing of the international search report

20 JUL 2000

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